# ADDITIONAL MONITORING OF THE CONCENTRATIONS OF METHYL BROMIDE AND CHLOROPICRIN IN THE AIR DOWNWIND FROM FIELDS DURING AND AFTER PREPLANT SOIL FUMIGATIONS (SHALLOW INJECTION)

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## SUMMARY

The concentrations of methyl bromide and chloropicrin in the downwind air were monitored during and after two preplant soil fumigations (shallow injection) in Orange County in 1983. In general, the concentrations of both methyl bromide and chloropicrin fluctuated throughout the time monitoring was done. There are no established standards for public exposure to these fumigants. The results obtained were compared to accepted work place standards. All results were below the Cal/OSHA 8-hour work place Permissible Exposure Limit (PEL) of 15 ppm for methyl bromide and 0.1 ppm (100 ppb) for chloropicrin. The concentrations of methyl bromide ranged from below the detectable limit (0.1 ug/10 L sample or 3 ppb) up to 814 ppb. The concen- trations of chloropicrin ranged from below the detectable limit (0.1 ug/10 L sample or 1 ppb) up to 81 ppb.

## INTRODUCTION

Methyl bromide and chloropicrin are toxicity Category I pesticides. Mixtures of the two chemicals are registered for use in California as a preplant soil fumigant. The mixture is used to kill weed and grass seeds, nematodes and other soil-borne organisms.

Methyl bromide is a colorless, tasteless, nonflammable gas which is odorless except at extremely high concentrations (2). It is known to cause damage to the lungs, nervous system, kidneys, and skin with sufficient dosage. The onset of symptoms from overexposure can be delayed for up to several hours. The Cal/OSHA Permissible Exposure Limit (PEL) for methyl bromide is 15 ppm for an 8-hour time-weighted average (TWA) in the work place environment. There is no established standard for nonwork place environments. The Cal/OSHA ceiling level (not to be exceeded) for methyl bromide is 50 ppm. The American Conference of Governmental Industrial Hygienists (ACGIH) has recommended a Threshold Limit Value (TLV) of 5 ppm and a Short-Term Exposure Limit (STEL) of 15 ppm.

Chloropicrin is a colorless oily liquid. The odor threshold is reported from 0.78 to 1.1 ppm (3, 4). Concentrations of 0.3 ppm result in painful irritation to the eyes in three to 30 seconds (1). No threshold level for eye irritation was found in the work place environment. There are no standards for nonworkplace environments. No Cal/OSHA ceiling has been set for chloropicrin, but using the guidelines in Title 8, Section 5155 of the California Administrative Code, 0.3 ppm would be the recommended maximum exposure concentration. The ACGIH has recommended a TLV of 0.1 ppm and a STEL of 0.3 ppm (1). These recommendations were made to provide freedom from eye irritation and prevent potential pulmonary changes.

The major use period of the methyl bromide/chloropicrin mixture as a soil fumigant to fallow fields is from early July to early October. The methyl bromide and chloropicrin are premixed in compressed gas cylinders by the registrant. The mixture is shank-injected into the soil approximately eight inches deep using a positive pressure closed system (pressurized with nitrogen gas). A one mil polyethylene tarp is automatically laid down over the soil behind the shanks. The tarp reduces the dissipation rate of the gases into the air which lessens the hazards to the workers and increases the overall efficacy of the gases.

## MATERIALS AND METHODS

Air samples were collected approximately 50 feet downwind from the fumigation site. Site adjustments were made as shifts in the wind direction became apparent (see Charts 1 & 2). The sampling periods lasted for one hour each at application site #1 and for approximately two hours each at application site #2.

Methyl bromide was trapped on charcoal sorbent tubes (SKC # 226-09, Lot 120), while the chloropicrin was trapped on two XAD-4 resin tubes (SKC #226-30-11-04, Lot 146). Separate MSA model C-210 portable pumps were used with each type of tube. The pumps were calibrated to draw 10 liters of air or less per sampling period. The pumps were calibrated at 150 ml of air/minute for sampling periods of one hour and at 75 ml of air/minute for sampling

periods of two hours. The counters on the C-210 portable pumps were also calibrated to determine the ml/count ratio. The counters were read before and after each sample period. The net count was multiplied by the ml/count ratio to determine the volume of air (in ml)/sample.

All samples were capped and placed on dry ice and shipped to the Department's laboratory for analysis. In the laboratory, the sampling tubes were divided into sections to determine if breakthrough occurred, indicating nonquantitative trapping of methyl bromide or chloropicrin. The charcoal tubes were separated into front and back sections with each analyzed separately. See Appendix 1 for the analytical method for methyl bromide. The chloropicrin sample was analyzed in two sections to detect the amount of breakthrough, if any, into the second section. The first section was the first tube and the second section was the second tube. See Appendix 2 for the analytical method for chloropicrin.

## RESULTS

There are no established standards for public exposure to these fumigants. The results obtained were compared to accepted work place standards. The data show the concentrations of methyl bromide in the downwind air to be significantly below the Cal/OSHA PEL of 15 ppm. In fact, all were below 1 ppm, with the highest concentration being 814 ppb. The corresponding data for chloropicrin showed the concentrations to be below the Cal/OSHA PEL of 0.1 ppm (100 ppb). The highest chloropicrin concentration found was 81 ppb. See Tables 1 through 4 for a summary of the data.

## DISCUSSION

Concerns have been raised about the hazards of methyl bromide and chloropicrin exposure to people living or working adjacent to fumigated fields. The objective of the study was to determine the concentrations of methyl bromide and chloropicrin in the air downwind from the fumigated fields. Monitoring sites were moved to compensate for changes in the wind direction. Although the protocol planned for 24 hours of continuous monitoring, rain following fumigation #2 caused the monitoring to be halted by mid-afternoon. It is not known what effect, if any, the rain had on the concentrations of methyl bromide and chloropicrin found in the air after the rain began.

The results of the methyl bromide monitoring in the air show concentrations ranging from 100 to 400 ppb downwind during the fumigation and for several hours after the end of the fumigation (see Graphs 1 & 3). The results also show that concentrations within this range are likely to occur the following morning as well.

The results of the chloropicrin monitoring generally show concentrations ranging from not detected up to 40 ppb. Like the methyl bromide results, some of the highest concentrations of chloropicrin were found the morning after the fumigation.

The relatively high concentration of the fumigants found in the morning is probably due to the relative lack of wind during the early morning hours. The lack of wind allows both fumigants to accumulate over the fumigated

field. When the wind picks up slightly, this accumulation moves downwind over adjacent areas.

The data produced by monitoring these two fumigations show that airborne concentrations of methyl bromide should not cause acute reactions to people living and/or working around fumigated fields. Although the concentrations of chloropicrin were at relatively safe levels, the possibility exists that people who are sensitive to chemicals could experience short periods of time when their eyes could be slightly irritated, depending on the concentration present and the individual's sensitivity. Analyses of the samples showed no breakthrough problems with either the charcoal (methyl bromide) or XAD-4 resin (chloropicrin) tubes. Concentrations of methyl bromide and chloropicrin in the breathing zone of fumigation workers were also monitored. The results are in the California Department of Food and Agriculture, Worker Health and Safety, Report HS-1175.

## CONCLUSIONS

The data indicate the concentrations of methyl bromide in the downwind air from field fumigations should not pose an acute health hazard under normal conditions. The data also indicate the concentration of chloropicrin in the downwind air would probably not cause problems to people living and/or working near fumigated fields. Sensitivity to chloropicrin and very brief periods of higher chloropicrin concentrations possibly could produce minor irritation (especially to the eyes). Concentrations of methyl bromide and chloropicrin in the air downwind the following morning may be found at comparable levels to those measured during the fumigation.

## REFERENCES


1. American Conference of Governmental Industrial Hygienists. 1980. Chloropicrin. Documentation of the Threshold Limit Values (4th Edition). Cincinnati.

2. American Conference of Governmental Industrial Hygienists. 1980. Methyl Bromide. Documentation of the Threshold Limit Values (4th Edition). Cincinnati.

3. Amoore, J. E. and E. Hautala. Odor as an Aid to Chemical Safety: Odor Thresholds Compared With the Threshold Limit Values and Volatilities for Industrial Chemicals (In Press).

4. National Institute for Occupational Safety and Health/Occupational Safety and Health Administration. 1981. Occupational Health Guidelines for Chloropicrin. Occupational Health Guidelines for Chemical Hazards. Washington, D.C.

## Table 1

**CONCENTRATIONS OF METHYL BROMIDE IN PARTS PER BILLION IN THE DOWNWIND AIR DURING AND AFTER PREPLANT SOIL FUMIGATION #1**

| Time | Site 1 | Site 2 | Site 3 | Site 4 | Site 5 |
|---|---|---|---|---|---|
| 0700-0800 | 329 | 396 | - | - | - |
| 0800-0900 | 174 | 274 | - | - | - |
| 0900-1000 | ND | ND | - | - | - |
| 1000-1100 | - | - | 262 | 299 | - |
| 1100-1200 | - | - | 258 | 123 | - |
| 1200-1300 | - | - | 323 | 197 | - |
| 1300-1400 | - | - | 247 | 192 | - |
| 1400-1500 | - | - | 226 | 147 | - |
| 1500-1600 | - | - | 219 | 109 | - |
| 1600-1700 | - | - | 195 | - | - |
| 1700-1800 | - | - | 141 | - | - |
| 1800-1900 | - | - | 54 | - | - |
| 1900-2000 | - | - | 24 | - | - |
| 2000-2100 | - | - | 21 | - | - |
| 2100-2200 | - | - | 74 | - | - |
| 2200-2300 | - | - | 4 | - | - |
| 2300-2400 | - | - | 2 | - | - |
| 2400-0100 | - | - | 78 | - | - |
| 0100-0200 | - | - | 27 | - | - |
| 0200-0300 | - | - | - | - | 344 |
| 0300-0400 | - | - | - | - | 340 |
| 0400-0500 | - | - | - | - | 241 |
| 0500-0600 | - | - | - | - | 353 |
| 0600-0700 | - | - | - | - | 189 |
| 0700-0800 | - | - | - | - | 113 |
| 0800-0900 | - | - | - | - | 45 |

**Table 2**

**CONCENTRATIONS OF CHLOROPICRIN IN PARTS PER BILLION IN THE DOWNWIND AIR DURING AND AFTER PREPLANT SOIL FUMIGATION #1**

| Time | Site 1 | Site 2 | Site 3 | Site 4 | Site 5 |
|---|---|---|---|---|---|
| 0700-0800 | 8 | 14 | - | - | - |
| 0800-0900 | 7 | 8 | - | - | - |
| 0900-1000 | ND | - | - | - | - |
| 1000-1100 | - | - | - | 23 | - |
| 1100-1200 | - | - | 21 | 14 | - |
| 1200-1300 | - | - | 31 | 21 | - |
| 1300-1400 | - | - | 34 | 24 | - |
| 1400-1500 | - | - | - | 25 | - |
| 1500-1600 | - | - | 23 | 17 | - |
| 1600-1700 | - | - | 24 | - | - |
| 1700-1800 | - | - | 17 | - | - |
| 1800-1900 | - | - | 6 | - | - |
| 1900-2000 | - | - | 3 | - | - |
| 2000-2100 | - | - | 3 | - | - |
| 2100-2200 | - | - | 6 | - | - |
| 2200-2300 | - | - | 1 | - | - |
| 2300-2400 | - | - | ND | - | - |
| 2400-0100 | - | - | 11 | - | - |
| 0100-0200 | - | - | 2 | - | - |
| 0200-0300 | - | - | - | - | 81 |
| 0300-0400 | - | - | - | - | 31 |
| 0400-0500 | - | - | - | - | 32 |
| 0500-0600 | - | - | - | - | 44 |
| 0600-0700 | - | - | - | - | 23 |
| 0700-0800 | - | - | - | - | 17 |
| 0800-0900 | - | - | - | - | 7 |

**Table 3**

**CONCENTRATIONS OF METHYL BROMIDE IN PARTS PER BILLION IN THE DOWNWIND AIR DURING AND AFTER PREPLANT SOIL FUMIGATION #2**

| Time | Site 1 | Site 2 | Site 3 |
|---|---|---|---|
| 0720-0920 | 814 | - | - |
| 0920-1120 | 448 | - | - |
| 1120-1320 | ND | 471 | - |
| 1320-1520 | 208 | 179 | - |
| 0520-0720 | 368 | 146 | - |
| 0720-0920 | - | - | 191 |

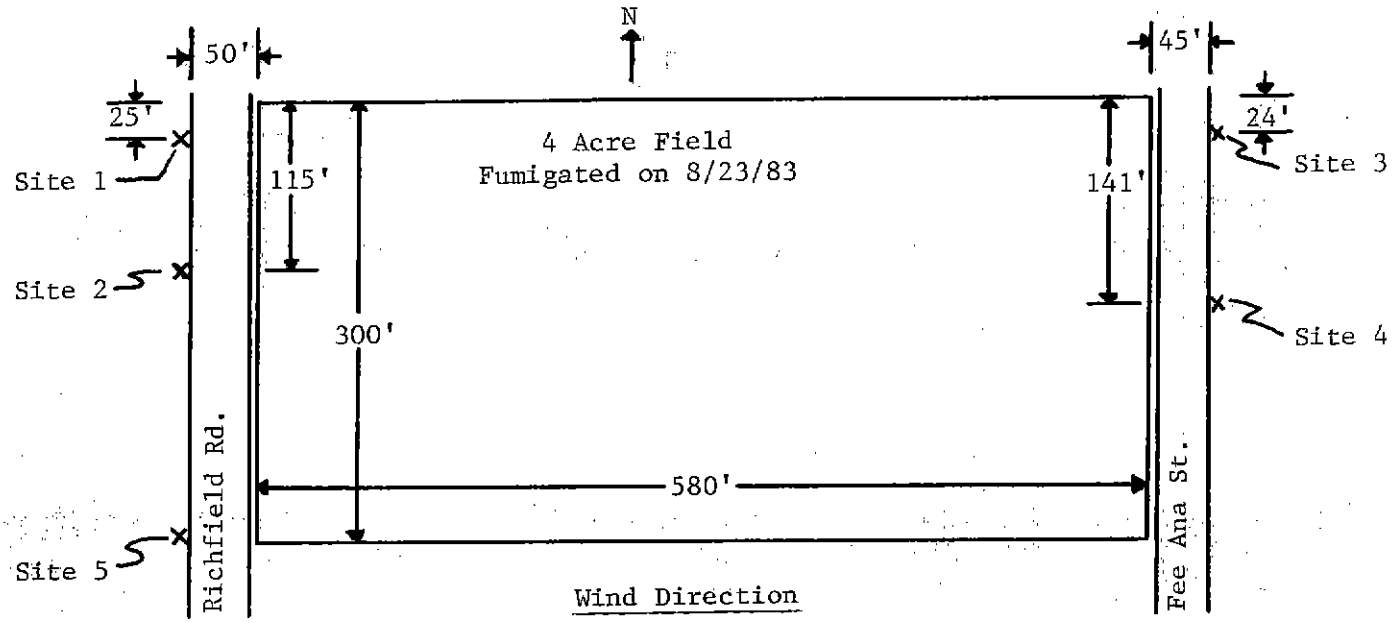
**Table 4**

**CONCENTRATIONS OF CHLOROPICRIN IN PARTS PER BILLION IN THE DOWNWIND AIR DURING AND AFTER PREPLANT SOIL FUMIGATION #2**

| Time | Site 1 | Site 2 | Site 3 |
|---|---|---|---|
| 0720-0920 | 16 | - | - |
| 0920-1120 | 15 | - | - |
| 1120-1320 | 16 | 33 | - |
| 1320-1520 | 13 | 30 | - |
| 0520-0720 | 40 | 18 | - |
| 0720-0920 | - | - | 20 |

**CHART 1**

**Fumigation # 1 Site Map**

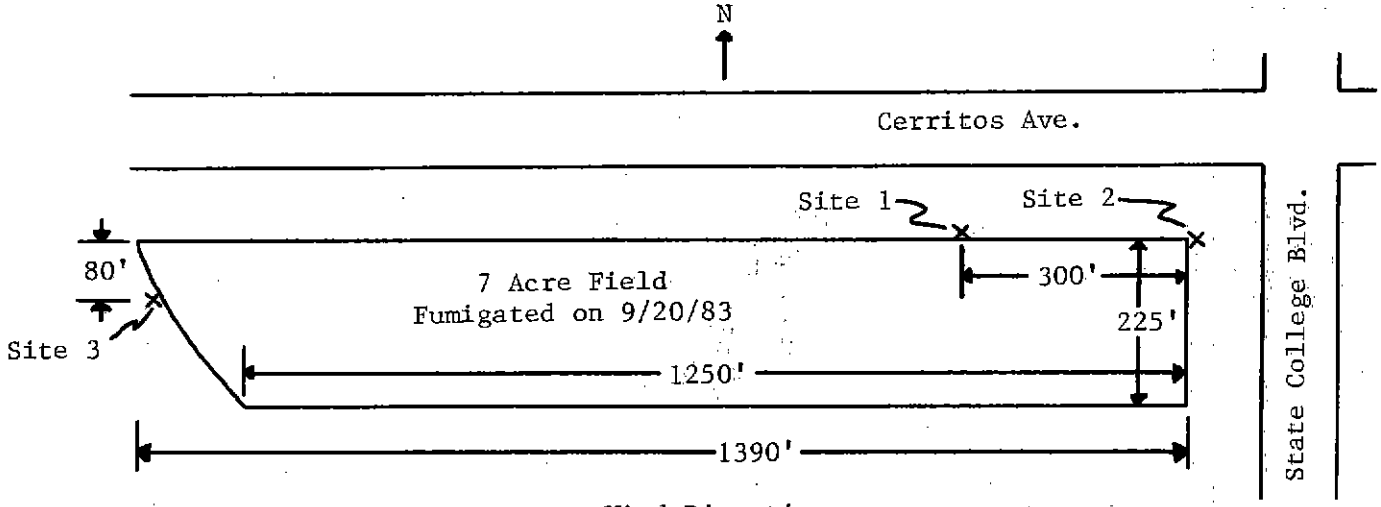



Wind Direction

8/23 0700 to 1010: ←
8/23 1010 to 8/24 0200: →
8/24 0200 to 0900: ←

**CHART 2**

**Fumigation # 2 Site Map**

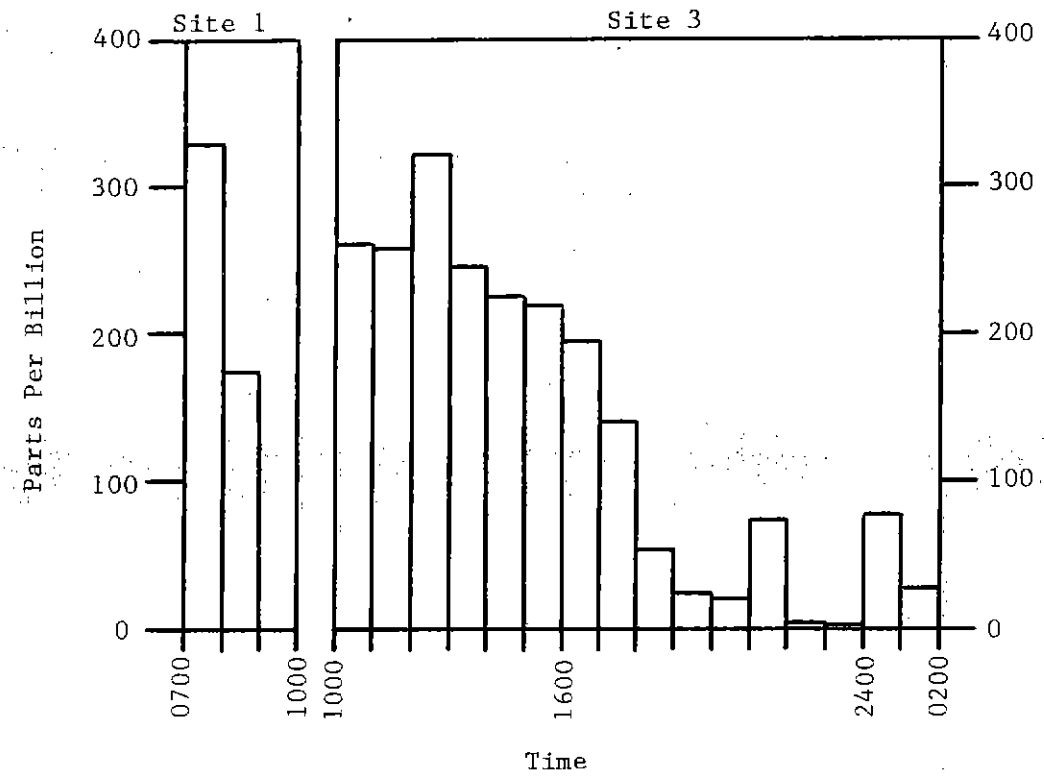


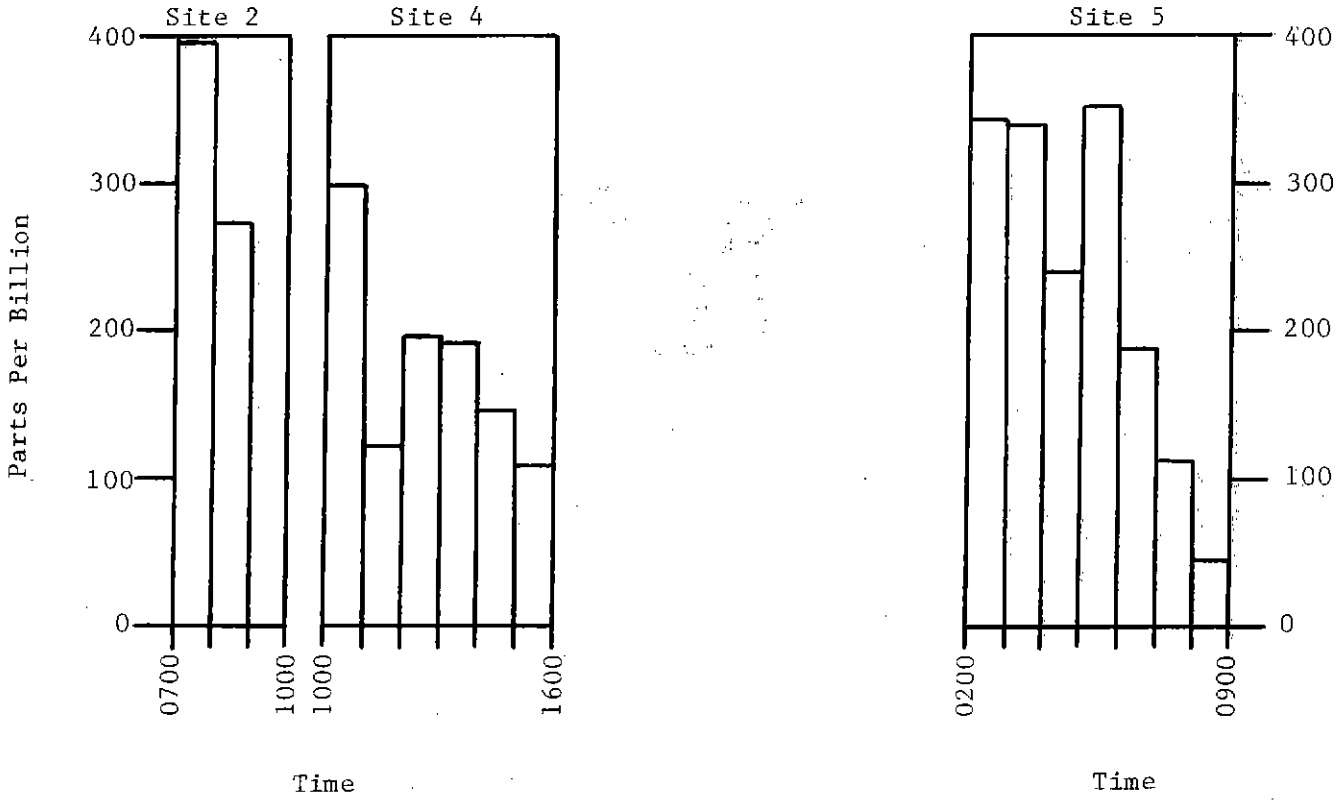

Wind Direction

9/20 0700 to 1520: →
9/21 0520 to 0720: →
9/21 0720 to 0920: ←

**GRAPH 1**

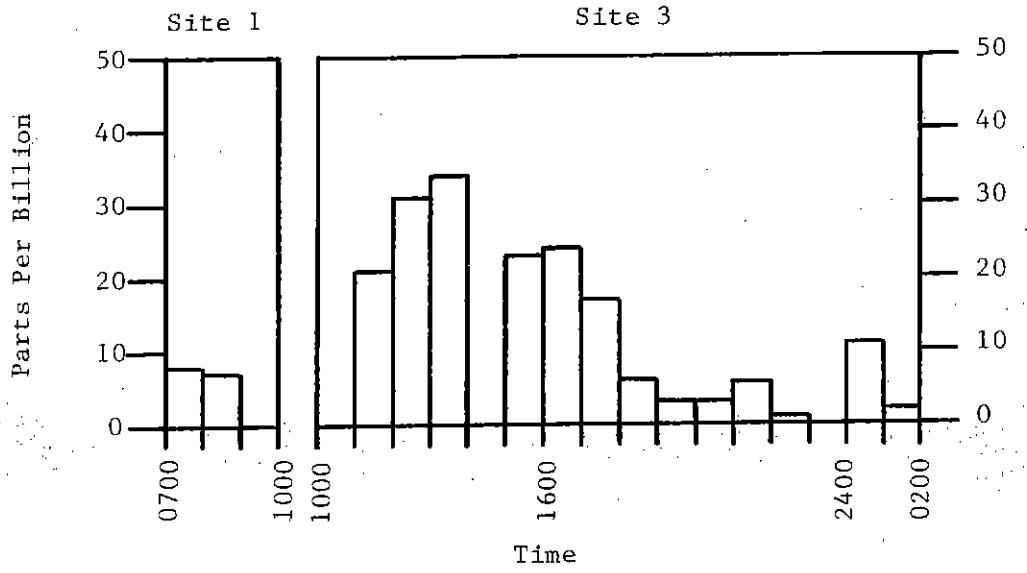
**Measured Concentrations of Methyl Bromide in the Downwind Air at Sites 1 Through 5 During and After Soil Fumigation #1**

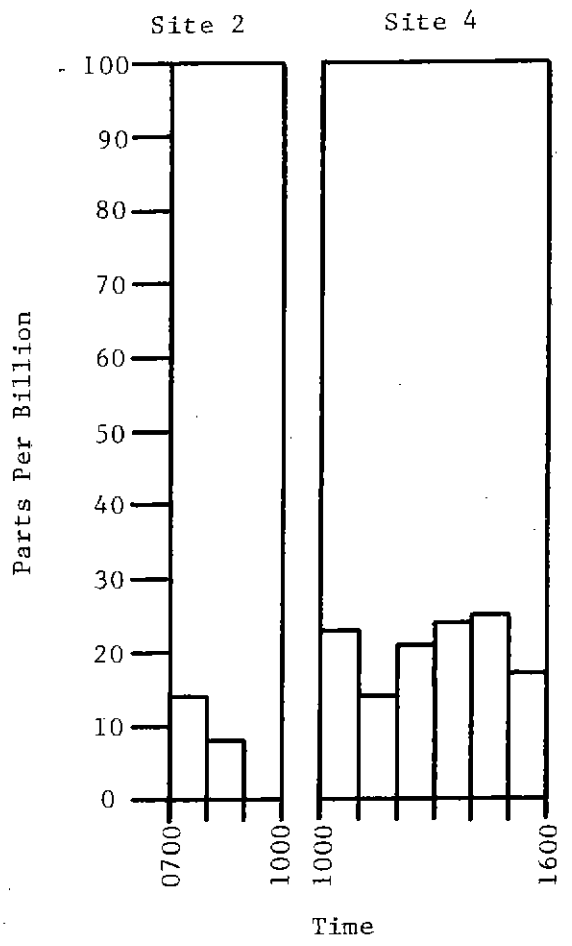


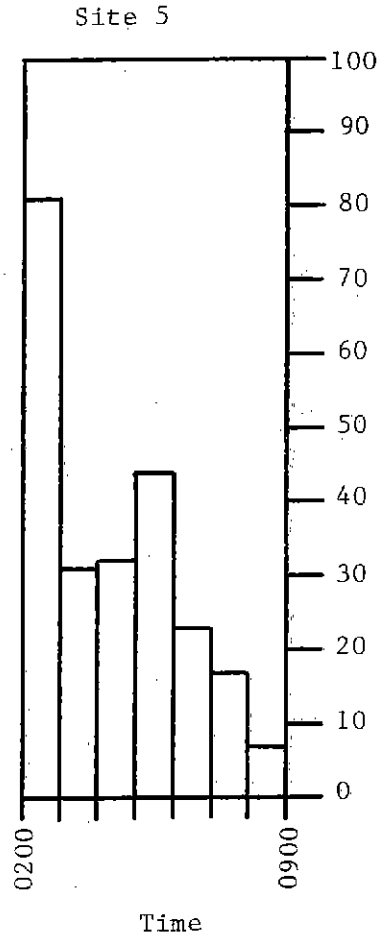



**GRAPH 2**

**Measured Concentrations of Chloropicrin in the Downwind Air at Sites 1 Through 5 During and After Soil Fumigation #1**

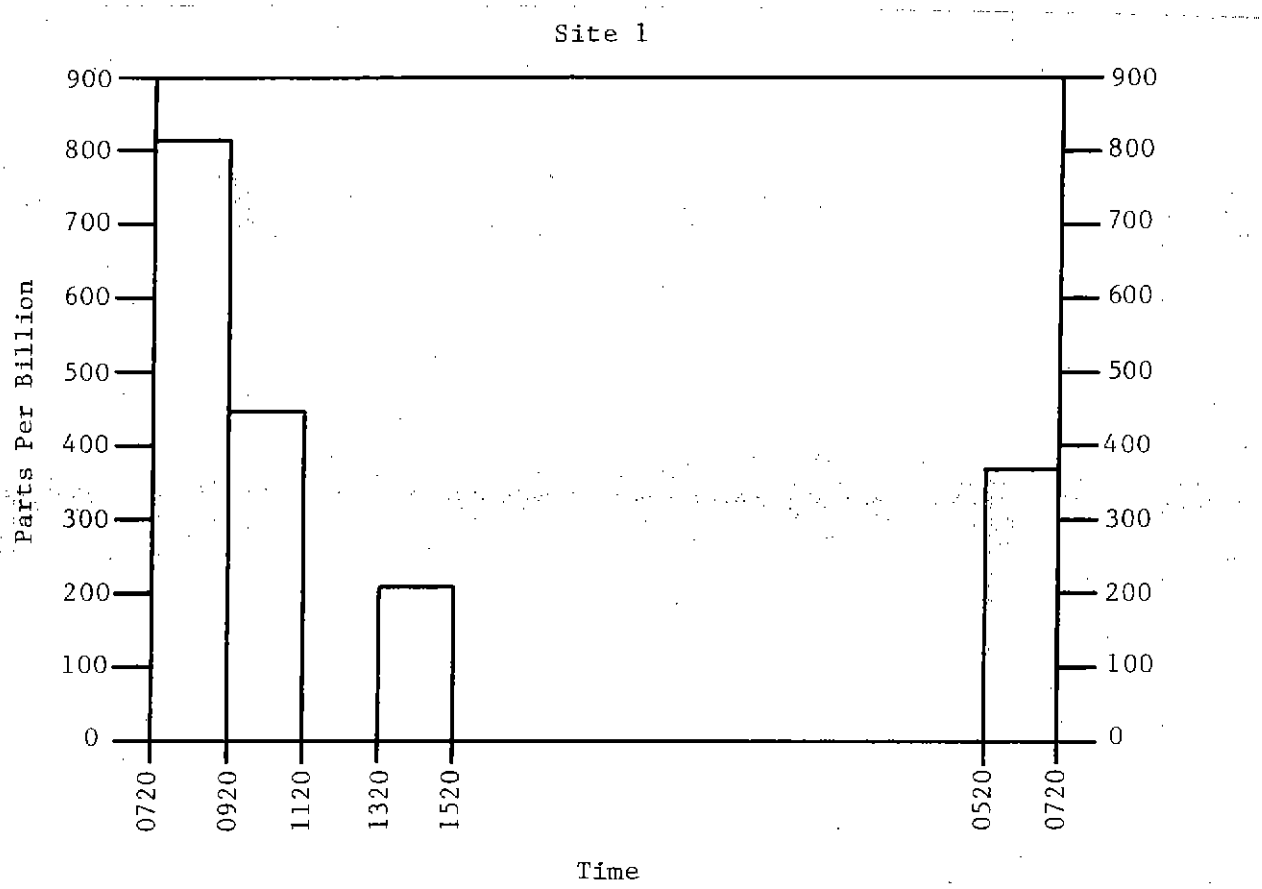


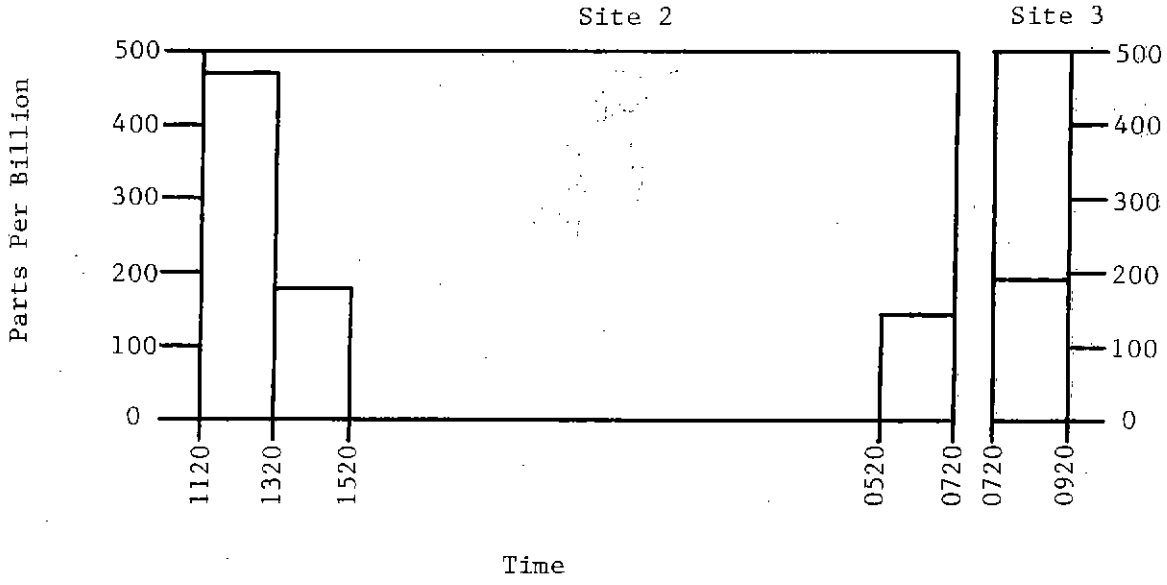



**GRAPH 3**

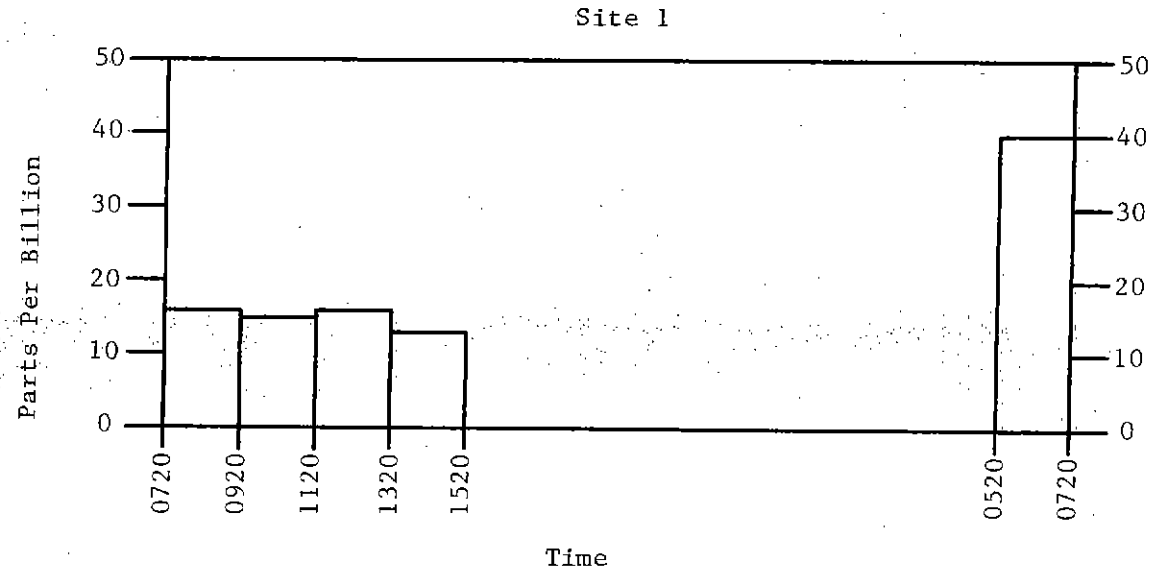
**Measured Concentrations of Methyl Bromide in the Downwind Air at Sites 1 Through 3 During and After Soil Fumigation #2**

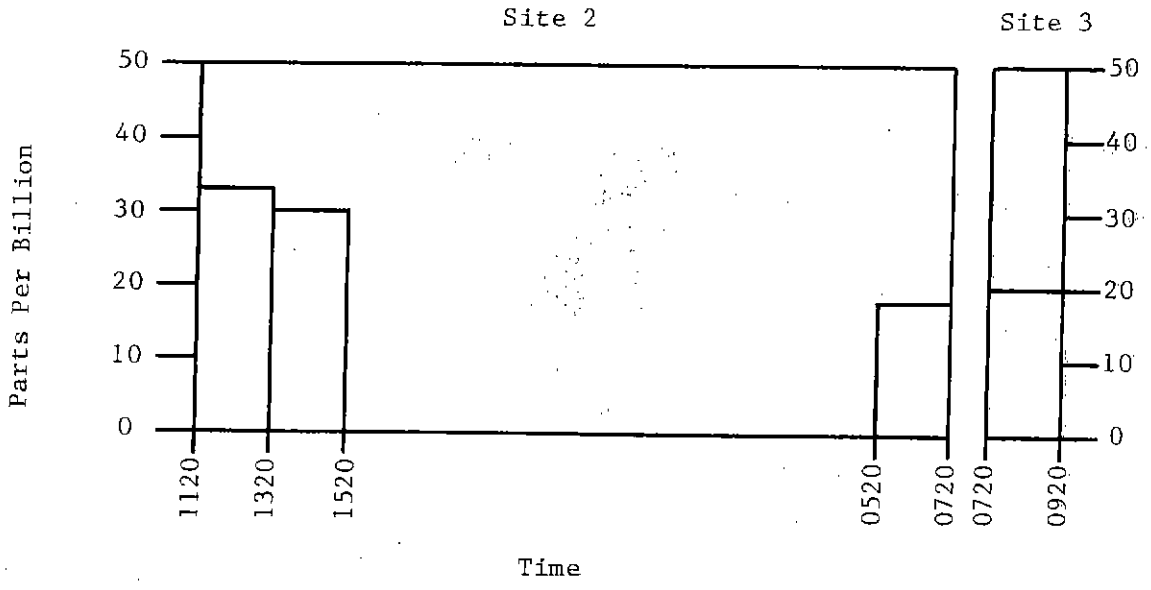


**GRAPH 4**

**Measured Concentrations of Chloropicrin in the Downwind Air at Sites 1 Through 3 During and After Soil Fumigation #2**



## APPENDIX 1

## DETERMINATION OF METHYL BROMIDE ON CHARCOAL TUBES

**SCOPE:**

This method is for the desorption and analysis of methyl bromide from charcoal air sampling tubes. It is intended solely for the use of the California Department of Food and Agriculture, Chemistry Laboratory Services.

**PRINCIPLE:**

Methyl bromide (MeBr) that has been adsorbed from the air onto activated charcoal is desorbed from the charcoal with ethyl acetate, diluted as needed and analytically determined by gas chromatography using flame ionization or electron capture detection.

**REAGENTS AND EQUIPMENT:**

1. Ethyl acetate, nanograde
2. Analytical grade methyl bromide
3. Approved and calibrated personal sampling pump
4. Charcoal tubes--SKC #226-09
5. Developing vials with teflon liners--SKC #226-02
6. Assorted microsyringes for preparing standards and gas chromatography
7. Assorted pipets
8. Volumetric flasks
9. Small triangular file for scoring glass tubes
10. Gas sampling bulb--Supelco 500 ml with septum (#2-2148)

**ANALYSIS:**

Interferences: High humidity may affect trapping efficiency.

1. Score each charcoal tube with a file in front of the first section of charcoal.
2. Break open the tube. Remove and discard the glass wool.

3. Transfer the charcoal in the upstream section to a labeled desorption vial which contains a known amount of nanograde ethyl acetate. 2-4 ml is suggested. Adding solvent to the charcoal may cause loss of MeBr.

4. Remove and discard the foam partition from the tube.

5. Transfer the second section of charcoal to a second labeled desorption vial which contains a known amount of nanograde ethyl acetate.

6. Allow the samples to desorb for one hour while rotating at 30 rpm.

7. Transfer an aliquot to a sample storage vial, label, and freeze until analysis time.

8. Determine by GLC.

**DETERMINATION OF DESORPTION EFFICIENCY:**

1. Inject a known amount of MeBr (one microgram to several milligrams) into the charcoal with a syringe and cap the tube with the supplied caps. The tube should be from the same lot that was used for the samples.

2. At least five tubes (preferably at levels covering the expected range) should be prepared in this manner and allowed to stand at least overnight to assure complete adsorption. A blank tube should be treated the same way except that no sample is added.

3. Analyze the tubes by the analytical procedure.

4. Desorption efficiency = $\frac{\text{Response sample - response blank}}{\text{Response standard}}$

The standard(s) should be the same amount as injected into the charcoal tubes. This eliminates standard variation errors.

**CALCULATIONS:**

1. Determine weight of MeBr present on charcoal tube sections by GLC analysis.

2. Correct this total weight of MeBr by subtracting any blank value present on the blank tube.

3. The corrected weight is divided by the desorption efficiency to obtain the final weight of MeBr present.

4. The volume of air sampled is converted to standard conditions of 25°C and 760 mm Hg.

$$VS = \frac{V \times P \times 298}{760 \times (T + 273)}$$

Where:

VS = Volume of air at standard conditions
V = Volume of air as measured
P = Barometric pressure in mm Hg
T = Temperature of air in °C

5. Calculate ppb in air from the above data.

$$\text{ppb (volume basis)} = \frac{ng \times 24.45}{VS \times 94.9} = \frac{ng}{VS} \times 0.2576$$

24.45 is the mole volume of MeBr at 25°C and 760 mm.
94.9 is the molecular weight of MeBr.

**GAS CHROMATOGRAPHIC CONDITIONS:**

Gas chromatograph with $Ni^{63}$, $H^3$, or flame ionization detector.

Temperatures - Injector: 125°C
Detector: Follow manufacturer's suggestions

Column: 20' x 1/8" O.D. nickel tubing
10% SP-2100 on 100/120 Chromosorb W-HP
70°C, 10 ml/min $N_2$ carrier gas
MeBr retention time is approximately 1.9 minutes

Column: 6' x 2 mm I.D. glass
80/100 Poropak Q
130°C, 30 ml/min $N_2$ carrier gas
MeBr retention time is approximately 1.4 minutes

Column: 20' x 1/8" O.D. nickel tubing
10% FFAP on 100/120 Chromosorb W-HP
70°C, ml/min $N_2$ carrier gas
MeBr retention time approximately 1.9 minutes

**REFERENCES:**


1. NIOSH Manual of Analytical Methods, Second Edition. Method S372. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

2. Determination of EDB on Charcoal Tubes, California Department of Food and Agriculture, Chemistry Laboratory Services, 3292 Meadowview Road, Sacramento, California 95832.

3. Malone, B., Analysis of Grains for Multiple Residues of Organic Fumigants. AOAC, 52, p. 800, 1969.

4. Clower, M., Modification of the AOAC Method for Fumigants in Wheat. FDA Laboratory Information Bulletin #2169, August 1978.

5. Mr. Mario Fraccia, Air Industrial Hygiene Lab, Berkeley, California. Personal Communication.

## APPENDIX 2

## THE ANALYSIS OF AIR SAMPLES FOR CHLOROPICRIN

**SCOPE:**

This analysis is for the determination of chloropicrin on XAD-4 resin air sample tubes.

**PRINCIPLE:**

Chloropicrin is trapped on XAD-4 resin tubes at the sampling site, frozen during transport to the lab, desorbed with ethyl acetate, and analyzed on a capillary GLC using electron capture detection.

**REAGENTS AND EQUIPMENT:**

1. Ethyl acetate--pesticide grade, checked for interferences
2. Appropriate glassware
3. Gas Chromatograph

Instrument: Hewlett Packard 5880 with ECD detector at 300°C.

Column: 30 M x .25 mm J&W 1701 at 40°C. Operated in split mode--approx. 100:1 split
Column pressure: 20 psi
Split flow: 40 ml/min

Injector: Split injector liner at 220°C.

Under these conditions chloropicrin elutes in 6.5 minutes.

Column: 12 ft x 2 mm 10% SP 2100 at 70°C and 35 ml/min Ar/Me

Under these conditions chloropicrin elutes in about 4 minutes.

**ANALYSIS:**

Break the XAD-4 tubes and place the resin in five ml vials containing four ml ethyl acetate. Desorb tubes for an hour on a rotator. Proceed to the GLC with no further preparation.

**DESORPTION COEFFICIENT:**

The desorption coefficient is 94% at the two microgram/spl level.

**CALCULATIONS:**

Results should be reported in ppb and mg/cu meter using the appropriate air sample calculations. The molecular weight of chloropicrin is 164.4. The concentration of analyte in the air sampled can be expressed in $mg/m^3$, which is numerically equivalent to micrograms per liter of air.

$$mg/m^3 = \frac{\text{mg analyte/sample x 1000}}{\text{liters of air sampled}}$$

The concentration in ppb can be expressed as follows:

$$ppb = mg/m^3 \times \frac{24.45 \times 760 \times (T + 273)}{MW \times P \times 298}$$

Where:

P = air pressure in mm Hg
T = air temperature in degrees C
24.45 = molar volume (L/mole) at 25°C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = NIOSH standard pressure in mm Hg
298 = NIOSH standard temperature--degrees Kelvin

**DISCUSSION:**

At the present time, a single sample consists of two tubes in series. The entire first tube is treated as the 'front' section, and the second tube is treated as two additional sections. This system was used to check out breakthrough. If the sample size is kept to 10 L or less, and the sample flow rate is about 200 ml/min, the breakthrough will be 10% or less.

Recoveries are 94% for levels of about 30 ppb, or two ug/spl.

**REFERENCES:**

1. Guide to Chemicals Used in Crop Production, Information Canada, p. 118, 1973. NIOSH Manual of Analytical Methods, Method S212, S104, 260.